Mercury (II) Removal Using CNTS Grown on GACs

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Abstract— **Elemental (metallic) mercury primarily causes health effects when it is breathed as a vapor where it can be absorbed through the lungs, at higher exposures there may be kidney effects, respiratory failure and death. This study aimed to study the performance of carbon nanotubes (CNT) grown on granular activated carbon (GAC) as an adsorbent for removal of mercury from aqueous solution. Due to its highly toxic effects to humans and environment, heavy metal concentrations in water are restricted by strict standards and reduced to the standard permitted. The effect of pH, agitation speed, contact time and CNT dosage was studied for optimal adsorption of mercury in the aqueous solution. Design Expert software was used to determine the number of runs and its variations, which are 18 runs. It was found that the optimal condition for mercury (II) ions adsorption occurred at adsorbent dosage of 5 mg, pH value of 5, contact time of 120 minutes and agitation speed of 150 rpm. The model resulted R^2= 0.8517 indicating 85.17% of the factors,which were pH, contact time,agitation speed and adsorbent dosage correlated to each other.**

Keywords— **Mercury, CNT-GAS, ANOVA, adsorption.**

I. INTRODUCTION

Heavy metals such as mercury, lead, nickel copper and cadmium have been proven to cause serious health effects on human [1]. Mercury had been widely used in many fields, such as medical, scientific research applications, and in amalgam material for dental restoration. It is used in lighting; electricity passed through mercury vapor in a phosphor tube produces short-wave ultraviolet light which then causes the phosphor to fluoresce, making visible light.

According to Torres [2], mercury is a well-known heavy metal pollutant of the aquatic environment, which is transformed to other more toxic species as methylmercury [3]. Many technologies were developed to avoid the throughput of mercury to the environment, however this element and its toxic species still cause many ecological problems due to wrong waste management by mining, electronic, chloro-alkali, etc. industries [4].

The first report pertaining to the toxicity of this metal and its compounds is probably in the works of Plenius Senior (23-79 A.D. During the Roman Empire, slavery at the Cinnabar mines was used as a terrible punishment for "disobedient" citizens. This was amounting to a slow, painful death [5]. Although mercury is useful for human, it still has its own disadvantages since human had suffered health problems due to the usage of mercury. Excessive ingestion on heavy metals can cause accumulative poisoning, cancer, nervous system damage and etcetera [6]. Therefore, there is a need to focus on the removal of mercury from water due to its toxicity to human health. Adsorption method is reported to be the most common method to remove mercury in wastewater because of its simplicity and cost-effectiveness [4].

Various adsorbents are normally used for this process such as iron oxides, activated carbon and filamentous fungal biomass. During the last years, there was a growing interest in the use of biomaterials for the sorption and preconcentration of heavy metals from water. Yeast biomass was tested for the speciation of methylmercury and Hg (II) [7]. Carbon nanotubes grown on granulated activated carbon (GAC) were applied since it is said to be a potential adsorbent for heavy metal removal in water treatment.

II. EXPERIMENTAL WORK

The following diagram explained the method used to remove the mercury from water. CNT-GACs were obtained from the Department of Biotechnology Engineering, International Islamic University Malaysia. Manufacturing of this material was done by previous postgraduate student. CNT-GACs were kept in a Bijou bottle at room temperature as the preservation procedure. The preparation of Mercury stock solution was done in order to produce stock solution with a concentration of 1mg/l. The glasswares used for the experiment were rinsed with 2% nitric acid in order to remove all the impurities that might present and also to prevent further adsorption of Mercury on the surface of walls of the glasswares.

N.A. Abu Osman et al. (Eds.): BIOMED 2011, IFMBE Proceedings 35, pp. 88–91, 2011.
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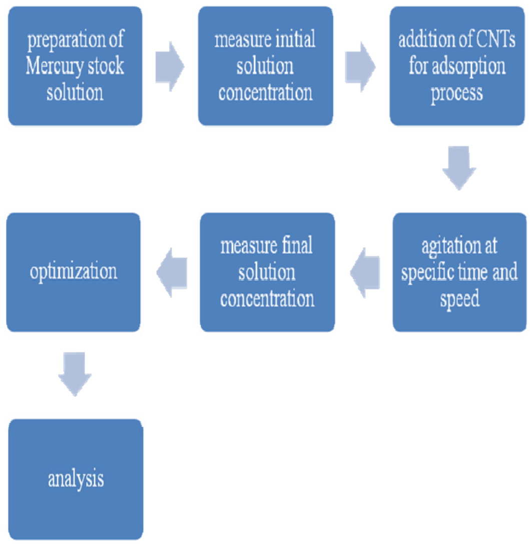


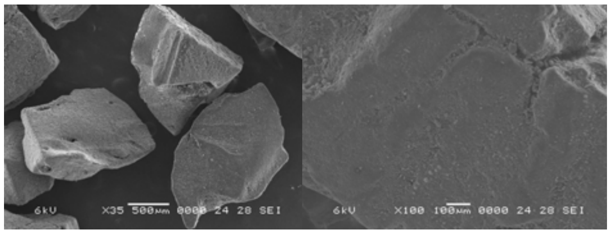
Fig. 1 Overall steps of experiment

A. *Experimental Design*

The experimental design was performed for optimization to determine the optimum value aqueous solution. This was done by using Design Expert 6.0.8 with different parameters as CNT dosages of 5-10 mg, agitation speed in rpm (50-150), pH (5-8), and contact time between 20-120 minutes. With two-level factorial and two replicates, the experiments will be conducted in 18 runs. The values for pH, agitation speed, contact time and adsorbent dosage were set to compare between the high and low rate. For the initial Mercury concentration, the value was chosen based on the factory effluents from several chloralkali plants in Europe, which is 1.6 mg/l.

III. RESULTS AND ANALYSIS

CNT and silicon structures are electrically conductive, thus they can be imaged using a conventional scanning electron microscope (SEM). In Figure 2, it can be observed that the CNT-GAC were scattered and not well-aligned. The layers of the wall cannot be seen clearly. After the adsorption experiment, it is observed that there were some black spots on the surface of the CNT-GAC. The spots showed that adsorption process had occurred on the CNT-GAC surface.



(a) (b)

Fig. 2 SEM images of CNT grown on GAC before adsorption experiment with varied magnifications; (a) x35 (b) x100

Table 1 Percentage removal of Mercury (II) ions

Run	Factor 1 A:pH	Factor 2 B:speed (rpm)	Factor 3 C:contact time (min)	Factor 4 D:adsorbent dosage (mg)	Response 1 Hg(II) concentration (mg/l)	% Removal
1	8.00	150.00	20.00	5.00	0.654	59.125
2	5.00	50.00	120.00	10.00	0.313	80.438
3	8.00	50.00	120.00	5.00	0.613	61.688
4	8.00	150.00	120.00	10.00	0.568	64.500
5	6.50	100.00	70.00	7.50	0.139	91.313
6	8.00	150.00	20.00	5.00	0.731	54.313
7	6.50	100.00	70.00	7.50	0.196	87.750
8	8.00	150.00	120.00	10.00	0.432	73.000
9	5.00	50.00	20.00	5.00	0.925	42.188
10	8.00	50.00	20.00	10.00	0.826	48.375
11	5.00	150.00	20.00	10.00	0.437	72.688
12	**5.00**	**150.00**	**120.00**	**5.00**	**0.031**	**98.063**
13	8.00	50.00	120.00	5.00	0.042	97.375
14	5.00	50.00	120.00	10.00	0.375	76.563
15	5.00	50.00	20.00	5.00	0.838	47.625
16	5.00	150.00	120.00	5.00	0.039	97.563
17	8.00	50.00	20.00	10.00	0.735	54.063
18	5.00	150.00	20.00	10.00	0.417	73.938

Run 12 have given the best result of mercury removal by using pH5, rpm 150, at 120 minutes and at 5 dosage of mercury.

A. *Modeling by Statistical Analysis*

Analysis of the result was done by using Design Expert 6.0.8. Information regarding the regression, correlation coefficients and standard deviations were also computed by using this software. The regression model relating the removal percentage of mercury is as follows:

Final Equation in Terms of Coded Factors:

Hg(II) concentration = +0.50+0.077 * A-0.085 * B-0.20 * C+0.014 * D+0.11 * A * B+0.035 * A * C+0.051 * A * D

Final Equation in Terms of Actual Factors:

Hg(II) concentration = +2.36249-0.22488* pH-0.010884 * speed-7.01417E-003 * contact time-0.082217* adsorbent dosage+1.41333E-003* pH * speed+4.73333E-004* pH * contact time+0.013533* pH * adsorbent dosage

where

A = pH; B= speed; C= contact time; D= adsorbent dosage

The value of correlation coefficient of R^2 and adjusted R^2 value determine the quality of the results, in which R^2 is equal to 0.8517 while adjusted R^2 is equal to 0.7364. Table 2 shows the value of R^2.

B. Analysis of Variance (ANOVA)

To investigate the relationship and between the response variable and independent variables, analysis of variance was used. The model resulted R^2= 0.8517 indicating 85.17% of the factors,which were pH, contact time,agitation speed and adsorbent dosage correlated to each other. The R^2 value also indicates that 14.83% of the variation was not explained by the model.

Table 2 P- and F Value for ANOVA of Hg(II) removal

Sources		**Sum of Squares**	**DF**	**Mean Square**	**F value**	**Prob > F**	
Model		1.07	7	0.15	7.39	0.0039	significant
	A	0.094	1	0.094	4.52	0.0624	
	B	0.12	1	0.12	5.55	0.0429	
	C	0.62	1	0.62	29.86	0.0004	
	D	3.306 E-003	1	3.306E -003	0.16	0.6992	
	AB	0.18	1	0.18	8.66	0.0164	
	AC	0.020	1	0.020	0.97	0.3502	
	AD	0.041	1	0.041	1.98	0.1926	
Curvature		0.19	1	0.19	9.38	0.0135	significant
Pure Error		0.19	9	0.021			
Cor Total		1.46	17				

From the analysis, the Model F-value of 7.39 implies the model is significant. There is only a 0.39% chance that a "Model F-Value" this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case B, C, AB are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model. The parameters involved in this study, which are pH, contact time, agitation speed and adsorbent dosage can be analyzed by graphical representation. One plot factor and 3-dimensional interaction plot were used to show the interaction between those parameters. The linear effect of changing the level of a single factor in the range of low (-1) and high (+1) levels was shown in one plot factor, while other factors are fixed at certain values. The 3-dimensional plot shows the interaction between the actual factors.

C. Comparative Analysis of Various Adsorbents

Table 3 Comparison of various adsorbents and its adsorbent capacity

Adsorbent	Adsorbent capacity	Reference
Cellulose of *Acetobacter xylinum*	1. 65µg/g(chlor-alkali wastewater 2. 80µg/g-synthetic wastewater	A.Rezaee et al.,2005
Cellulose carrier modified with polyethleneimine	288.0 mg/g	Navarro et al.,1996
Camel backbone	28.24 mg/g	Hassan SS et al.,2008
Activated carbon (Indian almond)	94.43 mg/g	Inbaraj & Sulochana,2006
Sago waste carbon	55.6 mg/g	Kadivelu,2004
CNT-GAC	6.405 mg/g	This study

Based on Table 3, it shows that there are many studies on the removal of Hg (II) using various types of adsorbent. However, the adsorbent capacity for each adsorbent is different due to the variation in the operating parameters (pH, agitation speed, dosage, temperature and many more). Thus, this comparative study was conducted to further understand the mechanism of adsorption and compare the types of adsorbents that were previously used to remove Hg (II).

IV. Conclusions

The effects of heavy metals such as lead, mercury, copper, zinc and cadmium on human health have been studied extensively. Excessive ingestion of them can cause accumulative poisoning, cancer, nervous system damage, etc. Since human beings are exposed to hazardous metal such as mercury, a great concern on how to overcome the effect should be investigated. Carbon nanotubes and activated carbon are found to be efficient as an adsorbent to remove heavy metal from wastewater. This study concentrates on the removal of heavy metals from wastewater by using carbon nanotubes grown on granulated activated carbon (GAC), where mercury was chosen as the heavy metal. The efficiency of the adsorption was determined in term of percentage removal.

The four parameters that were chosen to determine the optimization of the process are pH, agitation speed, contact time and also the adsorbent dosage used, which is the CNT grown on GAC. The results showed that the most significant factor contributing to the adsorption process was the contact time. This model term gives the highest F-value in

ANOVA analysis, which is 29.86. It is also shown that the four parameters are significant from the ANOVA analysis. From the result, the optimal conditions for mercury (II) ions removal occur at adsorbent dosage of 5 mg, pH 5, agitation speed of 150 rpm and contact time of 120 minutes.

ACKNOWLEDGMENT

The author acknowledge the financial help from the research grant EDW A10-160-0713 of IIUM.

REFERENCES

1. Kabbashi,N.A., Atieh,MA., Al-Mamun,A., Mirghami, Mohamed ES, Alam, Md.Z., & Yahya,N. (2008) Kinetic adsorption of application of carbon nanotubes for Pb(II) removal from aqueous solution. *Journal of Environmental Sciences,* 21, 539–544
2. Torres,J., Olivares,S., De La Rosa,D., Lima,L., Martinez,F.,Munita,C.S.,& Favaro,D.I.T.(1998).Removal of Mercury(II) and methylmercury from solution by tannin adsorbents. *Journal of Radioanalytical and Nuclear Chemistry*, Vol.240, p.361-365
3. Canstein,H.V, Li,Y., Timmis,K.N., Deckwer,W.-D.,& Wagner,D.B.(1999), Removal of Mercury from Chloralkali Electrolysis Wastewater by a Mercury-Resistant *Pseudomonas putida* Strain. *Applied and Environmental Microbiology,* 65(12), 5279–5284. South J, Blass B (2001) The future of modern genomics. Blackwell, London
4. Goyal,M., Bhagat,M., & Dhawan,R. (2009). Removal of mercury from water by fixed bed activated carbon columns. *Journal of Hazardous Materials*, 171, 1009–1015.
5. Pavlogeorgatos,G.,& Kikilias,V.(2003), The Importance of Mercury Determination and Speciation to The Health of The General Population. *Global Nest: The Int.Journal* ,4(2-3), 107-125
6. Zabihi,M., Ahmadpour,A., & Haghighi,A.A.,(2010) Studies on adsorption of mercury from aqueous solution on activated carbons prepared from walnut shell. *Journal of Hazardous Materials,* 174,251–256.
7. Sakamoto,H., Ichikawa,T.,Tomiyasu,T., & Sato,M.(2004). Mercury Concentration in Environmental Samples of Malaysia.*Faculty of Science,Kagoshima University*,37,83-90

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